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ADHESIVE RESIN COMPOSITION AND LAMINATE EMPLOYING SAME

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Specification

1. Title of Invention:

Adhesive Resin Composition and Laminate Employing Same

2. Claim

(1) An adhesive resin composition obtained by grafting an ethylenic unsaturated carboxylic acid or an anhydride of said carboxylic acid to a polyethylene polymer having a density of 0.91-0.86 g/cm³ and admixing a 0.02-0.3 equivalent of the hydroxide or salt of a periodic group Ia or IIa metal relative to the ethylene unsaturated carboxylic acid or carboxylic anhydride, or admixing the metal compound and a polyethylene polymer having a density of 0.91-0.86 g/cm³.

(2) The adhesive resin composition of claim 1 wherein said ethylenic unsaturated carboxylic acid or carboxylic acid anhydride is maleic anhydride.

(3) The adhesive resin composition of claim 1 or 2 wherein said metal compound is a metal compound comprising the hydroxide or salt of a periodic group Ia metal.

(4) The adhesive resin composition of any of claims 1 through 3 wherein (said adhesive resin composition is an interlayer adhesive for co-extrusion.)

¹ Numbers in the margin indicate pagination in the original.

(5) A laminate obtained by laminating between a gas barrier resin and a hydrophobic thermoplastic resin an adhesive resin composition obtained by grafting an ethylenic unsaturated carboxylic acid or an anhydride of said carboxylic acid to a polyethylene polymer having a density of 0.91-0.86 g/cm³ and admixing a 0.02-0.3 equivalent of the hydroxide or salt of a periodic group Ia or IIa metal relative to the ethylene unsaturated carboxylic acid or carboxylic anhydride, or admixing the metal compound and a polyethylene polymer having a density of 0.91-0.86 g/cm³.

(6) The laminate of claim 5 wherein said metal compound is the hydroxide or salt of a periodic group Ia metal.

(7) The laminate of claim 5 or 6 wherein said gas barrier resin is an ethylene-vinyl acetate copolymer saponified resin comprising a 20-55 molar percent ethylene component and having a degree of saponification of not less than 90 percent.

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(8) The laminate of any of claims 5 through 7 wherein said hydrophobic thermoplastic resin is polyethylene.

(9) The laminate of any of claims 5-8 wherein said laminate is a coextrusion laminate.

3. Detailed Description of the Invention

A. Field of Industrial Use

The present invention relates to an adhesive resin composition and to a laminate obtained by laminating an adhesive resin composition between a gas barrier resin, particularly an ethylene-vinyl acetate copolymer saponified resin, and a hydrophobic thermoplastic resin.

B. Prior Art and Its Problems

There have been marked changes in technology in the field of food packaging in recent years. For example, it is known that hydrophobic thermoplastic resins such as polyethylene are being increasingly employed in food packaging with the objective of achieving sanitation, an attractive exterior, and weight reduction that reduces transport costs. However, these polyethylene resins have low barrier properties with regard to oxygen, carbon dioxide, and the like. They are not suited to the long-term storage of foods, carbonated beverages, and the like, for which glass bottles and metal cans are largely employed. There are numerous problems in the form of the public harm done by the discarding of empty cans on the road and the cost required to recycle bottles. There is a need for substitute packaging materials.

Ethylene-vinyl acetate copolymer saponified resins with an ethylene component of 20-55 molar percent can be melt molded,

have high transparency, and have good gas barriers. These are good characteristics for use in food containers and packaging materials. However, they have drawbacks relating to other physical properties such as rigidity and moisture resistance, and are not fully satisfactory.

By contrast, hydrophobic thermoplastic resins, particularly ethylene resins, afford a balance between moldability, impact resistance, and rigidity and have good sanitation properties. However, their gas barrier to oxygen and carbon dioxide, for example, is inadequate and their use in food containers and packaging materials is limited.

Accordingly, to achieve food containers and packaging materials having both the good gas barrier properties of ethylene-vinyl acetate copolymer saponified resins and the good mechanical characteristics of hydrophobic thermoplastic resins such as polyethylene resin, the two resins could conceivably be laminated. However, these resins have almost no compatibility with each other and it is impossible to obtain a laminate simply by thermal adhesion.

It is well known that an ethylenic unsaturated carboxylic acid or the anhydride of such a carboxylic acid can be grafted to polyethylene resin in a composition of ethylene-vinyl acetate copolymer saponified resin and a hydrophobic thermoplastic resin

such as polyethylene resin to obtain a laminate having adhesion. However, there are numerous problems relating to industrial application with the adhesive resins obtained by grafting an ethylenic unsaturated carboxylic acid or an anhydride component of such a carboxylic acid to an ethylenic resin. For example, the greatest problem is that of molding speed. In industrial applications, molding speed is a major factor affecting manufacturing costs. That is, even with good basic adhesive performance, since adhesiveness decreases as the molding rate rises, the molding speed must be made extremely slow. This results in excessively high manufacturing costs, sometimes imposing major limitations on industrial application. Since various molding conditions affect each other, the pull rate cannot be independently determined. However, for example, the greater the pull rate, the more rapid the molding rate, and the lower the manufacturing cost, which is significant from the perspective of industrial application. For the adhesive resin obtained by grafting an ethylenic unsaturated carboxylic acid or the anhydride of such a carboxylic acid to polyethylene resin, there are often substantial limitations on the pull rate of the extruded laminate resin. That is, although there is adequate adhesiveness when the pull rate is low, adhesiveness often

decreases when pulling is conducted at high speed, constituting a major impediment to industrial application.

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Patent Publication Shō 39-6810 discloses a method of manufacturing an ionic copolymer by reacting a copolymer obtained from one or more α -olefins and one or more α , β -ethylenic unsaturated carboxylic acids having one or two carboxyl groups, with one or more ionic metal compounds dissolved in water. Therein, it is stated that it is desirable for a suitable base copolymer to be placed in the presence of a monoethylenic unsaturated monomer capable of yielding a third copolymer, or in the absence thereof, for ethylene to be directly copolymerized with a monocarboxylic acid monomer. The neutralization of at least 10 percent of the acid radicals in the base copolymer with metallic ions such as Na^+ to obtain a product having rubber elasticity, flexibility, thermal stability, rigidity, abrasion resistance, and other physical properties that are desirable in solids as well as melt fluidity is described, and the superiority of such a product is claimed. It is further disclosed that the base copolymer can be obtained by grafting an α -olefin and an acid monomer to a polyolefin base. However, this method is described as being suited to the use of polyolefins obtained from olefins having a molecular weight greater than that of ethylene,

such as propylene and butene-1. The desirable application of polyethylene copolymer as the polyolefin is not disclosed.

Further, the cited invention is a product the physical properties of which are improved in resins having a melt index (MI) of 0.1-100 g/10 min. Only resins having MIs of 100 g/10 min or greater are disclosed for use as adhesives and laminate products.

However, in the ionic copolymer obtained by reacting a copolymer obtained from one or more α -olefins and one or more α , β -ethylenic unsaturated carboxylic acids having one or two carboxyl groups with one or more ionic metal compounds dissolved in water, perhaps because the carboxyl groups are in the main chain, almost no adhesiveness to gas barrier resins is exhibited. Further, the resin obtained by using a polyolefin obtained from propylene or butene-1 as the base copolymer, grafting on an acid monomer, and neutralizing with metallic ions exhibits no adhesiveness to polyethylene. Still further, there are problems such as when the MI is 100 g/10 min or greater, the MI becomes excessively large and molding is precluded. Thus, a practically useful adhesive resin is not obtained.

C. Problems to Be Solved by the Present Invention

In light of such problems, the present inventors, based on the required characteristics of adhesive resins during industrial co-extrusion, conducted extensive research into the relation between the various physical properties and coextrusion adhesiveness of adhesive resins to molding properties. They obtained an adhesive resin composition having adequate adhesiveness even when high-speed pulling was conducted during industrially rapid coextrusion molding, and obtained with this composition a laminate having a good external appearance.

D. Means of Solving the Problems

In the present invention, extensive research was carried out on the relation between the various physical properties of adhesive resins and coextrusion adhesiveness and molding properties based on the characteristics that are required of an adhesive resin during industrial coextrusion. As a result, it was discovered that by employing an adhesive resin composition obtained by grafting a specific compound to a polyethylene polymer of specific density, and then incorporating a specific metal compound within a specific range, it was possible to achieve adequate adhesiveness in a laminate of good external appearance even during high-speed pulling in industrially high-speed coextrusion molding; the present invention was devised on that basis.

That is, the (present invention) is an adhesive resin composition obtained by grafting an ethylenic unsaturated carboxylic acid or an anhydride of said carboxylic acid to a polyethylene polymer having a density of $0.91-0.86 \text{ g/cm}^3$ and admixing a 0.02-0.3 equivalent of the hydroxide or salt of a periodic group Ia or IIa metal relative to the ethylene unsaturated carboxylic acid or carboxylic anhydride, or admixing the metal compound and a polyethylene polymer having a density of

0.91-0.86 g/cm³; the present invention is also a laminate obtained using this adhesive resin composition.

E. Effect of the Invention

In the adhesive resin composition of the present invention, a modified polyethylene resin of specific density is employed to achieve the properties of both the adhesiveness and high-speed moldability required of coextruded adhesive resins. Further, not only does the laminate obtained have a good external appearance, but it also has good mechanical characteristics and gas barrier properties, rendering it extremely useful in food containers and packaging materials.

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The most important feature of the present invention is that the density is within a prescribed range. Grafting an ethylene unsaturated carboxylic acid or the anhydride of such a carboxylic acid to a polyethylene copolymer having a density of 0.91-0.86 g/cm³ yields an adhesive resin capable of high-speed extrusion molding. The reason for this is not entirely clear. However, the crystallinity of the resin is thought to be a contributing factor. The effect of the present invention is not produced in copolymers with a density of 0.93-0.97 g/cm³ obtained by controlling crystallinity by copolymerizing vinyl acetate or ethyl acrylate; an α -olefin such as propylene, butene-1, hexene-

1, 4-methylpentene-1, or octene-1; and ethylene. This fact is quite surprising, is difficult to infer, and the present invention is difficult to devise from facts widely known by those skilled in the art, such as the fact that a laminate having adhesiveness can be obtained in a combination of ethylene-vinyl acetate copolymer saponified resin and a hydrophobic thermoplastic resin such as polyethylene resin by graft polymerization of an ethylene unsaturated carboxylic acid or the anhydride of such a carboxylic acid with polyethylene resin.

The next most essential feature is that stable molding is made possible even under harsh molding conditions by admixing a metal compound comprised of a 0.02-0.3 equivalent weight of the hydroxide or salt of a periodic group Ia or group IIa metal relative to the grafted ethylenic unsaturated carboxylic acid or anhydride component of such a carboxylic acid. The reason for this is not entirely clear. However, it is thought that the blending in of a metal compound comprised of the hydroxide or salt of a periodic table group Ia or group IIa metal within a prescribed range is related to the chemical reaction or chemical interaction at the interface between the adhesive resin composition layer and the hydrophobic thermoplastic resin layer, and/or the interface between the adhesive resin composition layer and the gas barrier resin layer in the step of coextrusion

molding, particularly during hot melting. This is entirely unpredictable from the above description relating to improvement in solid states due to metal ions, and was quite unexpected.

F. More Specific Description of the Present Invention

The most significant characteristic of the present invention is the use of a polyethylene copolymer having a density of 0.91-0.86 g/cm³ as the base. When the density exceeds 0.91 g/cm³, the effect of the present invention in the form of adequate adhesiveness during high-speed molding is not achieved, and polyethylene copolymers having a density of less than 0.86 g/cm³ are undesirable in that passing properties during the manufacturing process are inadequate and industrially stable feeding is precluded. To better achieve the effect of the present invention, the use of polyethylene polymer having a density of 0.905-0.87 g/cm³ as base is desirable. The method of manufacturing such a polyethylene polymer is not specifically limited. However, for example, one method is to (copolymerize ethylene and an α -olefin) at a polymerization temperature of 10-80°C with a Ziegler catalyst. (α -Olefins having 3-8 carbon atoms can be employed; examples are: propylene, butene-1, hexene-1, 4-methylpentene-1, and octene-1) Although the copolymerization proportion varies with the type of α -olefin, 7-30 molar percent is normally employed. Further, various dienes such as butadiene,

1,4-hexadiene, 1,5-hexadiene, vinyl norbornene, ethylidene norbornene, and dicyclopentadiene may be added and copolymerized as the third monomer. Examples of commercially available compounds are Toughmer A-4085, Toughmer A-4090, Toughmer P-0180, and Toughmer P-0480, sold by Mitsui Sekiyu Kagaku Co., and Flexresin DFDA-1137 NT7 and Flexresin DFDA-1138 NT, sold by Nippon Unika Co.

Examples of the (ethylenic unsaturated carboxylic acid or carboxylic anhydride employed) in grafting are: maleic acid, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic anhydride, itaconic anhydride, and other ethylenic unsaturated carboxylic acids and their carboxylic anhydrides. Of these, (maleic anhydride is preferred.) During grafting, it can be simultaneous cografted with comonomers such as ethylene, styrene, vinyl

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acetate, and vinyl ether. A graft level of 0.001-6 weight percent is suitable, but 0.01-5 weight percent is preferred from the perspectives of adhesiveness and molding properties.

The grafting method is not specifically limited. However, one method is to place an ethylenic unsaturated carboxylic acid or an anhydride of such a carboxylic acid and an organic peroxide compound such as dibenzoyl peroxide, dibutyl peroxide, dicumyl

peroxide, t-butyl perbenzoate, t-butyl hydroperoxide, or cumenehydroperoxide in the presence of a polyethylene copolymer and heat the compounds so that they undergo chemical bonding. For example, the reaction may be conducted in the presence or absence of a solvent such as benzene, toluene, xylene, chlorobenzene, t-butylbenzene, or cumene at a temperature of 100-240°C. Conducting the reaction in the presence of a solvent such as toluene or xylene at a temperature of 110-200°C is preferred because a uniform product is obtained.

In the practice of the present invention, (it is necessary) to incorporate a metal compound comprised of the hydroxide or salt of a periodic group Ia or IIa metal in a 0.02-0.3 equivalent quantity relative to the ethylenic unsaturated carboxylic acid or anhydride of such a carboxylic acid into the graft copolymer obtained as set forth above. The incorporation of such a metal compound widens the temperature range over which the various portions of the molding machine can be set, prevents the denaturation of resin remaining within the molding machine, and yields an extremely good coextrusion molded product. When the quantity of metal compound added is less than a 0.02 equivalent, the effect is not marked. When added in a quantity exceeding a 0.3 equivalent, the adhesive resin develops color, fluidity deteriorates, and the material is not suited for molding.

Examples of metal compounds comprised of the hydroxides or salts of periodic group Ia or IIa metals are sodium carbonate, lithium carbonate, magnesium carbonate, sodium acetate, sodium hydroxide, potassium hydroxide, calcium hydroxide, and magnesium hydroxide. Of these, sodium carbonate, sodium acetate, sodium hydroxide, potassium hydroxide, and other metal compounds comprised of the hydroxides or salts of periodic group Ia metals are employed with preference, with sodium hydroxide being the compound of greatest preference. This tendency is most apparent when the gas barrier resin is an ethylene-vinyl acetate copolymer saponified resin.

The modified copolymer obtained by incorporating a metal compound comprised of the metal hydroxide or salt in a 0.02-0.3 equivalent quantity relative to the ethylenic unsaturated carboxylic acid or anhydride of such a carboxylic acid into the copolymer obtained by grafting an ethylenic unsaturated carboxylic acid or an anhydride of such a carboxylic acid onto a polyethylenic polymer having a density of 0.91-0.86 g/cm³ in the present invention has adequate properties as is and can be employed industrially, or, when needed, can be blended with ethylene polymer having a density of 0.91-0.86 g/cm³ for use. In that case, although the blending ratio of modified copolymer and polyethylene polymer varies with the characteristics of the denatured copolymer and the polyethylene polymer, from the

perspectives of manufacturing cost and molding properties, the blending ratio is desirably 1:99, more desirably from 2:98 to 40:60, and still more desirably, from 5:95-30:70.

(Other additives normally incorporated into thermoplastic resins may be employed in the adhesive resin composition) of the present invention. (Examples of such additives) are antioxidants, ultraviolet-absorbing agents, plasticizers, antistatic agents, lubricants, and fillers. These may be blended in to the extent that they do not inhibit the effect of the present invention. Specific examples of additives are given below. Antioxidants: 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-p-creosol, 4,4'-thiobis-(6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, octadecyl-3-(3'-5-di-t-butyl-4'-hydroxyphenyl)propionate, and 4,4'-thiobis-(6-t-butylphenol). Ultraviolet-absorbing

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agents: ethyl-2-cyano-3,3-diphenyl acrylate, 2-(2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, and 2-hydroxy-4-octoxybenzophenone. Plasticizers: dimethyl phthalate, diethyl phthalate, dioctyl phthalate, wax, liquid paraffin, and

phosphoric acid ester. Antistatic agents: pentaerythritol monostearate, sorbitan monopalmitate, oleic acid sulfate, polyethylene oxide, and carbowax. Lubricants: ethylenebisstearoamide and butyl stearate. Colorants: carbon black, phthalocyanine, quinaclidone, indoline, azo dyes, titanium oxide, and Bengala. Fillers: glass fiber, asbestos, mica, and blastonite.

The ethylenic unsaturated carboxylic acid or anhydride of such a carboxylic acid that is grafted onto the polyethylene polymer having a density of 0.91-0.86 g/cm³, the content thereof, the metal compound comprised of the hydroxide or salt of a periodic group Ia or IIa metal, and the content thereof that are employed in the present invention may be of one type [and level] or mixtures of two or more types [and levels].

Examples of means of mixing the various components to obtain the composition of the present invention are: ribbon blenders, high-speed mixers, kneaders, mixing rolls, Banbury mixers, and extruders.

Ethylene-vinyl acetate copolymer saponified resin, nylon 6, nylon 6-6, nylon 6-12, and other polyamide resins can be employed as the gas barrier resin employed in the laminate of the present invention. Of these, ethylene-vinyl acetate copolymer saponified resins having an ethylene component content of 20-55 molar

percent and a degree of saponification of not less than 90 percent are preferred. Ethylene-vinyl acetate copolymer saponified resins treated with boric acid, borax, or some other boron compound; silicon-containing olefin unsaturated monomers; α -olefins; N-vinylpyrrolidone; and other third components can be copolymerized with ethylene and vinyl acetate and saponified to obtain modified resins that also have melt molding properties. So long as the compound does not diminish the various physical properties of the gas barrier resin, the effect of the present invention will be achieved.

Any resin capable of being hot melt molded can be employed as the hydrophobic thermoplastic resin; resins of preference are polyethylene, polypropylene, polyamide, saturated polyester, polycarbonate, vinyl chloride, polystyrene, ethylene-vinyl acetate copolymer resins, and ethylene-acrylic acid ester copolymer resins. The resin of greatest preference is polyethylene.

Examples of polyethylene resins are given below.

I. High-pressure polyethylene: a resin polymerized in the presence of a radical initiator at a pressure of at least 1,000 atmospheres.

II. Medium-pressure polyethylene: a resin polymerized at 30-40 atmospheres at 100-150°C in the presence of a catalyst such as Cr_2O_3 .

III. Low-pressure polyethylene: a resin polymerized at 0-7 atmospheres at 60-80°C with a catalyst in the form of triethyl aluminum mixed with titanium tetrachloride.

IV. LLDPE: A resin obtained by copolymerizing an α -olefin by solution polymerization or vapor phase fluidized bed polymerization.

The configuration of the laminate obtained by laminating the adhesive resin composition between a gas barrier resin and a hydrophobic plastic resin in the present invention can be a three-resin, three-layer A/B/C configuration; or a symmetrical or asymmetrical three-resin five-layer configuration such as A/B/C/B/A, C/B/A/B/C, A/B/C/B/A', or C/B/A/B/C' (where A and A' denote gas barrier resins, B denotes the adhesive resin composition, and C and C' denote hydrophobic thermoplastic resins). Further, multiple-resin multiple-layer configurations in which multiple layers of any of A, B, and C are employed are also possible. Methods used to form the laminate include lamination within a die and lamination outside a die with hot adhesion by pressing. Methods of

lamination within a die are preferred. Extrusion molding by the T-die method and ring die method are the methods of preference. However, the direct blow molding method and the injection blow molding method may also be suitably employed. The laminate obtained in this manner has both good gas barrier properties and good mechanical characteristics and is useful in food containers (cups, bottles) and packaging materials. Further, the laminate thus obtained may be rendered more useful by steps such as monoaxial or biaxial orientation, deep drawing, and blow molding. (The laminate obtained by the present invention may also be laminated with a synthetic resin film, metal, paper, or the like.)

The present invention is described below in greater detail through embodiments.

G. Embodiments

Embodiments 1-4

One hundred weight parts of Toughmer A-4085 (a polyethylene resin having a density of 0.88 g/cm^3 and an MI (190°C , 2160 g) of 3.6 g/min, manufactured by Mitsui Sekiyu Kagaku Co.) and 12 weight parts of maleic anhydride were dissolved in 720 weight parts of purified toluene and maintained at 180°C . To this solution was continuously added with stirring over a period of 2.0 hr 100 weight parts of purified toluene solution in which 1.3 weight parts of cumenehydroperoxide had been dissolved. A post

reaction was conducted for another 30 min once the addition had been completed. Following cooling, the reaction solution was poured into a large quantity of acetone to precipitate the polymer. The polymer obtained was purified by precipitation using purified toluene as solvent and acetone as nonsolvent. This product contained 2.1 weight percent of maleic anhydride component.

An aqueous solution comprising a specific quantity of sodium hydroxide (NaOH) was uniformly added to the polymer thus obtained and the mixture was partially dried. The mixture was then pelletized by melt kneading in an extruder equipped with vent while simultaneously removing volatile material under reduced pressure, yielding an adhesive resin composition comprising modified copolymer.

A prescribed quantity of the adhesive resin composition thus obtained was dry blended with the above-described Toughmer A-4085 and pelletized by melt kneading in an extruder, yielding an adhesive resin blended composition.

The vinyl acetate component of the ethylene-vinyl acetate copolymer, comprising 67 molar percent, was 99.6 percent saponified to obtain ethylene-vinyl acetate copolymer saponified resin of $[n]=1.11$ (in phenol/water = 85/15 mixed solution, 30°C, dl/g). This resin was employed as gas barrier resin and Mirason

27 (low-density polyethylene, MI=2.0 g/10 min, made by Mitsui Sekiyu Kagaku Co.) as hydrophobic thermoplastic resin to obtain a laminate by the following method.

An extruder I with an internal diameter of 120 mm, an extruder II with an internal diameter of 60 mm, and an extruder with an internal diameter of 90 mm were prepared. A feed block three-resin, five-layer coextrusion device was employed in which each of two melt materials were branched into two layers in extruders I and II, after which the resin from extruder II and the resin from extruder I were sequentially merged with the resin layer melt extruded by extruder III. Hydrophobic thermoplastic resin (C) was fed to extruder I, adhesive resin composition (B) was fed to extruder II, and gas barrier resin (A) was fed to extruder (A). Coextrusion was conducted at a die temperature of 220°C and a draw rate of 25 m/min to produce a three-resin, five-layered film of C/B/A/B/C (30/6/15/6/30 μ). The external appearance and peeling strength of this film were measured.

Embodiments 1 and 2, in which 0.05 equivalent quantities of NaOH were added relative to the grafted maleic anhydride, yielded molded products with good external appearance and adequate adhesive strength. Embodiments 3 and 4, in which 0.1 equivalent quantities of NaOH were added, yielded molded products with extremely good external appearance and adequate adhesive

strength. The peeling strength dropped hardly at all relative to when only modified copolymer adhesive resin composition was employed when the modified copolymerization adhesive resin composition content in the blended composition was 20 percent. The results are given in Table 1.

Comparative Examples 1-4

With the exception that the Toughmer A-4085 was replaced with Mirason 12 (density = 0.927 g/cm³, MI=3.0, Mitsui Sekiyu Kagaku Co.), coextrusion molding was conducted in the same manner as in Embodiments 1-4. The

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molded products obtained had good external appearance, but had low adhesive strength and peeled readily, rendering them of little commercial value. The results are given in Table 1.

With the exception that the quantity of NaOH was varied, the same procedure was followed as in Embodiments 1-4. In Comparative Examples 5 and 6, in which no NaOH was added, there were numerous irregularities on the surfaces of the molded products, the thickness thereof was uneven, and adhesive strength was uneven, rendering them of little commercial value. When a 1.0 equivalent quantity of NaOH was added, the metal-modified copolymer developed a brown coloration (Comparative Example 7) and it was impossible to uniformly mix the blended composition of

this metal-modified copolymer resin and Toughmer A-4085. Not only were there numerous brown spots, but the entire product had a brown coloration (Comparative Example 8), rendering the product of little commercial value; no coextrusion molding was conducted. The results are given in Table 1.

With the exception that Toughmer A-4085 was employed in the (B) adhesive resin layer, the same procedure was followed as in Embodiment 1 to obtain a laminated film. The external appearance of the film was good, but it had extremely low adhesive strength and peeled readily, rendering it of little commercial value.

Embodiments 5 and 6

With the exceptions that Flexresin DFDA-1138NT (density = 0.90 g/cm³, MI = 0.4 g/10 min, made by Nippon Unikā Co.) was employed in place of Toughmer A-4085, the quantities of maleic anhydride and cumenehydroperoxide employed were changed, and a 0.14 equivalent quantity of potassium carbonate (K₂CO₃) was employed in place of NaOH, adhesive resin compositions comprising 2.4 percent maleic anhydride components were prepared by the same methods as in Embodiments 1-4.

The above-obtained adhesive resin composition and Toughmer P-0180 (density = 0.88 g/cm³, MI = 4.5, made by Mitsui Sekiyu Kagaku Co.) were dry blended in a ratio of 10:90 as the (B) layer resin.

The vinyl acetate component comprising 56 molar percent of the ethylene-vinyl acetate was 99.5 percent saponified, yielding an ethylene - vinyl acetate copolymer saponified resin of $[\eta] = 0.96$ (in phenol/water = 85/15 mixed solution, 30°C, dl/g). This was employed as gas barrier resin (A), and Mirason 151 (low-density polyethylene, MI=2.0, made by Mitsui Sekiyu Kagaku Co.) was employed as hydrophobic thermoplastic resin (C).

An extruder I with an internal diameter of 60 mm, an extruder II with an internal diameter of 40 mm, and an extruder III with an internal diameter of 90 mm were prepared. A flat-die, three-resin, three-layer coextrusion device was employed in which the melt material from each of the extruders was spread within a single die by means of a manifold, and then merged within the die and laminated. Hydrophobic thermoplastic resin (C) was fed to extruder I, adhesive resin composition (B) was fed to extruder II, and gas barrier resin (A) was fed to extruder III. Coextrusion was conducted at a die temperature of 220°C and a pull rate of 20 m/min to prepare a three-layer C/B/A (50/8/15 μ) film. The film obtained had a good external appearance. Testing of peeling strength revealed adequate adhesive strength. The results are given in Table 2.

Embodiments 10-11

With the exceptions that Ultozecks 3055R (LLDPE, density = 0.935 g/cm³, made by Mitsui Sekiyu Kagaku Co.) was employed in place of Flexresin DFDA-1138NT and Ultozecks 2020L (LLDPE, density = 0.920 g/cm³, made by Mitsui Sekiyu Kagaku Co.) was employed in place of Toughmer P-0180, the same procedure was followed as in Embodiments 5 and 6. The molded products obtained exhibited good external appearance, but had extremely poor adhesive strength and tended to peel, rendering them of little commercial value. The results are given in Table 2.

Comparative Example 12

With the exception that a 10:90 mixture of Flexresin DFDA-1138NT and Toughmer P-0180 was employed as the adhesive resin, molding was conducted in the same manner as in Embodiment 7 to obtain a laminate film. The laminate film exhibited good external appearance but had extremely poor adhesive strength and tended to peel, rendering it of little commercial value. The results are given in Table 2.

Table 1

| | Equivalent quantity of NaOH added | Content of modified copolymer adhesive resin composition in blended composition | Laminate film | |
|-----------------|-----------------------------------|---|-------------------------------------|---|
| | | | External appearance | Peeling strength ¹⁾ (kg/cm) |
| Embodiment 1 | 0.05 | 100 | Good | 0.2 |
| Embodiment 2 | 0.05 | 20 | Good | 0.3 |
| Embodiment 3 | 0.1 | 100 | Extremely good | 0.3 |
| Embodiment 4 | 0.1 | 20 | Extremely good | 0.3 |
| Comp. Example 1 | 0.05 | 100 | Good | 0.08 |
| Comp. Example 2 | 0.05 | 20 | Good | 0.06 |
| Comp. Example 3 | 0.1 | 100 | Good | 0.07 |
| Comp. Example 4 | 0.1 | 20 | Good | 0.05 |
| Comp. Example 5 | 0 | 100 | Highly irreg. | 0.1-0.2 |
| Comp. Example 6 | 0 | 20 | Highly irreg. | 0.1-0.2 |
| Comp. Example 7 | 1.0 | 100 | Not molded due to strong coloration | |
| Comp. Example 8 | 1.0 | 20 | Not molded due to strong coloration | |

1) Peeling strength: Measured at center of film.

T peeling: 20 mm/min, 20°C, 65% RH

Table 2

| | Equivalent quantity of K_2CO_3 added | Content of modified copolymer adhesive resin composition in blended composition | Laminate film | |
|------------------|--|---|---------------------|---|
| | | | External appearance | Peeling strength ¹⁾ (kg/cm) |
| Embodiment 5 | 0.14 | 100 | Good | 0.3 |
| Embodiment 6 | 0.14 | 10 | Good | 0.2 |
| Comp. Example 10 | 0.14 | 100 | Good | 0.01 |
| Comp. Example 11 | 0.14 | 10 | Good | 0.01 |

1) Peeling strength: Measured in direction of extension at center of sheet
T peeling: 20 mm/min, 20°C, 65% RH